

OBSERVATIONS ON THE RARE EARTHS:

- I. FRACTIONAL PRECIPITATION OF THE CERIUM
GROUP EARTHS BY ELECTROLYSIS
- II. SOLUBILITY OF RARE EARTH OXALATES IN
NITRIC ACID
- III. SEPARATION OF CERIUM

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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COOPERATION WITH THE GEORGE W. WOODS LABORATORY OF THE UNIVERSITY OF ILLINOIS
OBSERVATIONS ON THE RARE EARTHS. XXV. I
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BY ELECTROLYSIS. II. SOLUBILITY OF RARE EARTH
OXALATES IN NITRIC ACID.

BY J. W. WOODS WITH H. C. EMMETT

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part of a series of experiments. J. W. Woods is partial recipient of the grant
made for the degree of Doctor of Philosophy in the Graduate School of the University of
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Thoms and others, Trans. American Chem. Soc., 37, 121 (1915); 37, 1223 (1916); 40, 171
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

**OBSERVATIONS ON THE RARE EARTHS. XXVII. I.
FRACTIONAL PRECIPITATION OF THE CERIUM GROUP EARTHS
BY ELECTROLYSIS. II. SOLUBILITY OF RARE EARTH
OXALATES IN NITRIC ACID¹**

BY J. W. NECKERS WITH H. C. KREMERS

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I. Fractional Precipitation of the Cerium Group Earths by Electrolysis

Electrolysis of neutral salt solutions of the rare earths will cause the formation of hydroxide at the cathode. Due to difference in basicities of the rare earth elements, a fractionation may be effected in this manner. Dennis and his co-workers² electrolyzed solutions of the rare earths using

¹ Part of a thesis submitted by J. W. Neckers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

² Dennis and others, *THIS JOURNAL*, 37, 131 (1915); 37, 1963 (1915); 40, 174 (1918).

a platinum anode and a mercury cathode. They effected separations of lanthanum from praseodymium and erbium from yttrium. Both nitrate and chloride solutions were used.

Brinton³ has recently determined the P_H values of several of the rare earth solutions at the point at which the hydroxide began to precipitate. The values of 6.83, 7.00, 7.05 and 8.35 are given for samarium, neodymium, praseodymium and lanthanum hydroxides, respectively. A confirmation of Brinton's values is shown in the electrolytic fractionation here described. Approximately 8% solutions were used.

A potential of 6 to 7 volts was found to give the best results.

The anode was made of platinum and was isolated by means of a porous porcelain cup.

A mercury cathode was always employed. Glass containers were used for cells. The electrolyte was stirred during electrolysis. The hydroxide fractions formed in most cases filtered fairly well although at times their gelatinous nature caused trouble. The following series of fractionations are reported.

Series I

Fifteen liters of 8% solution of lanthanum and praseodymium chlorides were used. Tabulated results are given in Table I.

TABLE I
LANTHANUM-PRASEODYMIUM

No.	Time, hrs.	Voltage, v.	Current, amp.	Wt. of oxide, g.	Color of oxide	Remarks
1	7	6	3.5	Manganese impurity
2	5	6	3.0	25	Chocolate brown	High % of Pr
3	1.5	5.8	4.8	17	Chocolate brown	High % of Pr
4	1.3	6.2	5.0	15	Chocolate brown	High % of Pr
5	1.5	6	3.8	18	Chocolate brown	High % of Pr
6	3	6.2	1.4	14	Medium brown	50% Pr 50% La
7	4	6.0	1.2	17	Light brown	20% Pr 80% La
8	6	6.2	1.4	22	Buff brown	5% Pr 95% La
9	6	6.5	1.0	18	Light buff	3% Pr 97% La
10	5	7.0	0.9	14	Light buff	1% Pr 99% La
11	5	6.2	.9	10	Light buff	1% Pr 99% La
12	4.5	7.2	1.1	15	Light buff	1% Pr 99% La
Residue				457	Light buff	99% La

³ Brinton, *J. Chem. Soc.*, 127, 2110 (1925).

Series II

The process was next applied to a mixture of all of the metals of the cerium group with a very small percentage of the yttrium group metals also present. An approximately 8% solution of 11.5 liters' volume was used under the same conditions as in Series I. A tabulation of the data follows.

TABLE II
CERIUM GROUP

No.	Time, hrs.	Voltage, v.	Current, amp.	Wt. of oxide, g.	Color of oxide	Remarks
1	7.5	6.8	0.9	14	Medium brown	Nd, Yt group, Sa, 5% Pr
2	23	7.0	1.3	49	Medium brown	Nd, Yt group, Sa, 5% Pr
3	10	7.0	3.0	41	Dark brown	50% Nd, 40% Pr, 10% Sa
4	9	7.0	3.3	23	Chocolate brown	50% Nd, 45% Pr, 5% Sa
5	14	7.0	2.7	36	Chocolate brown	50% Nd, 50% Pr
6	18	6.3	2.2	32	Chocolate brown	50% Nd, 50% Pr
7	17	6.5	2.3	36	Chocolate brown	50% Nd, 50% Pr
8	22	6.4	2.1	26	Chocolate brown	50% Nd, 50% Pr
9	18	7.0	2.3	27	Chocolate brown	50% Nd, 50% Pr
10	23	6.9	1.9	22	Chocolate brown	50% Nd, 50% Pr
11	24	7.4	1.7	29	Medium brown	35% Nd, 35% Pr, 30% La
12	27	7.0	1.7	30	Light brown	50% La, 25% Pr, 25% Nd
13	36	7.0	0.9	22	Buff	80% La, 10% Pr, 10% Nd
14	39	7.0	1.0	20	Buff	90% La, 5% Pr, 5% Nd
15	40	7.0	1.0	21	Light buff	98% La, 1% Pr, 1% Nd
16	39	7.0	1.1	15	Light buff	99% La, 1% Pr
17	35	7.2	1.2	12	Light buff	99% La, 1% Pr
18	40	7.0	1.1	11	White	100% La
19	36	7.2	1.1	10	White	100% La
20	59	7.0	1.1	12	White	100% La

Although samarium and the yttrium group metals concentrate in the first fractions, it appears possible to obtain only an efficient concentration of lanthanum.

Series III

This series was similar in composition to Series II except that the conductivity was increased threefold by the addition of 5% sodium chloride. The speed of electrolysis was thus increased correspondingly with no decrease in efficiency of separation.

Series IV

To apply this method to a more difficult separation, 12.5 liters of an 8% solution of praseodymium and neodymium chlorides (with 5% of sodium chloride) was electrolyzed. No appreciable separation or concentration occurred although several small fractions were precipitated at both ends of the series.

Discussion of Results

It appears possible to separate rare earths by electrolysis of neutral solutions only when the P_H values are separated by more than 0.25. The values given by Brinton³ are thus substantiated.

It is possible that a more efficient separation might be obtained by using more dilute solutions and much smaller amperages. Under such conditions the method would become less practicable.

II. Solubilities of Rare Earth Oxalates in Nitric Acid

Sarver and Brinton⁴ have recently determined the solubilities of several rare earth oxalates in nitric, hydrochloric and sulfuric acids at 25°.

Since there is considerable difference in solubility of the oxalates at room and at elevated temperatures, it seemed desirable to have solubility data taken at more elevated temperatures. Such data might be of value in a further study of methods of fractionation. Solubilities were accordingly run in mixtures of nitric and oxalic acids.

The solubility tests were carried out in 500cc. Florence flasks with long necks and covered with close fitting heavy watch glasses. A temperature of $90 \pm 2^\circ$ was maintained by means of a slightly modified steam-bath. Temperatures of 25° were maintained by ordinary methods. Excess oxalate was added to 150 cc. of the nitric acid contained in the flasks as described. Thirty-six hours with frequent shaking was considered long enough to establish equilibrium. For analysis, two 50cc. quantities of the solutions were withdrawn with a pipet, to the tip of which an efficient filter was attached, evaporated to dryness and ignited in porcelain.

TABLE III
SOLUBILITY OF OXALATES AT 90°
Grams of oxide from 100 cc. of solution

Normality of nitric acid	Oxalic acid, %	La	Pr	Nd	Sm	Dy	Yt
0.779	...	0.4421	0.3871
1.25	0.8707
1.558	...	1.2377	1.0764
2.337	1.8467
2.50	1.9571	1.8779	1.8458	1.3180
3.75	...	4.6670
5.00	...	10.4160	6.8825	6.7788	5.6750	4.8470	3.0135
0.779	5	0.0302	0.0275
1.25	5	0.0915
1.558	5	0.3083	0.1639
2.337	5	.7517	.6932
2.50	5	0.6760	0.5457	0.4215	0.4315
3.75	5	3.5260
5.00	5	9.3907	5.2339	5.1263	4.1520	3.4135	1.4515

⁴ Sarver and Brinton, *THIS JOURNAL*, 49, 943 (1927).

The solubility determinations made at 25° were in practical agreement with those published by Sarver and Brinton and hence need not be given here. The determinations made at 90° in nitric acid of various strengths and also in the presence of oxalic acid are given in Table III.

Discussion of Results

The determination of solubilities in 1.25 *N* acid was discontinued after it was found that the solubility was so small that no practical use could be made of such data. At 90°, especially in the 5 *N* acid solutions, it was found that the solution reached no definite saturation point. The solubility of the oxalate seemed to be proportional to the length of time that the excess solid salt was in contact with the solution. This was shown by the fact that neodymium oxalate in contact with the 5 *N* acid for a few hours yielded 5.7060 g. of oxide from 100 cc. of the solution while if it stood for three days the oxide weighed 8.8596 g. This is probably due to the formation of oxalonitrates and the data under the hot, concentrated acid may well be called a comparison of the rate of decomposition rather than of the solubility. (The solubility, however, is a function of the rate of decomposition.) Therefore, to obtain data which would, in a graphic form, show a comparison of the solubilities, the different oxalates were submitted simultaneously to the same solubility treatment, under like conditions for the same length of time. The data resulting from the procedure are those used in the 5 *N*, 90° series.

It is observed that the solubilities of the oxalates at 90° is of the same order as at 25°. From these data it may also be gathered that the separation of lanthanum from praseodymium is feasible by fractionation of the oxalates. Very little separation of the other members of the cerium group might be expected. Both of these facts have been proved by actual trial in this Laboratory. The separation of yttrium from holmium might also be feasible by this method.

Summary

1. It has been found possible to separate lanthanum from praseodymium and the other cerium group earths by fractional electrolytic precipitation. Addition of 5% of sodium chloride increases the conductivity, and thus the rate of precipitation, threefold without impairing the efficiency of the fractionation. Other separations in the cerium group are not feasible by this method.

2. The solubility of the oxalates of lanthanum, praseodymium, neodymium, samarium, dysprosium and yttrium has been determined in 1.25, 2.50 and 5.00 *N* nitric acid at 90°. A corresponding series of determinations has also been made with 5% oxalic acid added to the nitric acid.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XXVIII. THE SEPARATION OF CERIUM

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The separation methods applied to cerium are quite different from those usually applied to the rare earths. Cerium when oxidized to the quadrivalent state assumes properties sufficiently different from the other trivalent earths to effect a quantitative separation.

The oldest method using this property is that of Mosander² who used chlorine or bromine to oxidize the cerium. Other methods are the neutral permanganate process proposed by Stapff³ and perfected by Roberts,⁴ and the neutral potassium bromate method proposed by James.⁵ From the standpoint of the preparation of cerium free from other earths or the complete removal of cerium from the other earths, the first method is inefficient due to the necessity of several successive treatments with chlorine, making the process slow. The neutral permanganate method is rapid but does not yield pure cerium. The cerium dioxide precipitates along with the manganese dioxide, giving a very bulky precipitate which carries down with it considerable quantities of other rare earths. The potassium bromate method yields pure cerium but is very slow and expensive; long-continued boiling and excess of reagent are necessary.

One method of oxidation reported to be quite rapid is electrolytic oxidation. Knorre⁶ reported the oxidation of cerous sulfate by ammonium persulfate with the precipitation of a basic sulfate. Consequently, oxidation of cerous sulfate anodically might lead to the precipitation of ceric cerium due to the formation of persulfate around the anode. Bricout⁷ also reports the precipitation of ceric dichromate by the electrolysis of a slightly acid solution of cerous chromate. These two reports and others give a possibility of a cerium separation by anodic oxidation.

Experimental

(1) **Anodic Oxidation.**—Solutions of cerium earths containing 30% of cerous cerium were electrolyzed using graphite electrodes. Electrolysis of the nitrates, chlorides and sulfates of the above solutions in

¹ This paper represents part of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

² Mosander, *Ann.*, **48**, 210 (1843).

³ Stapff, *J. prakt. Chem.*, [1] **79**, 258 (1860).

⁴ Roberts, *Am. J. Sci.*, [5] **31**, 350 (1911).

⁵ James, *THIS JOURNAL*, **33**, 1326 (1911); **34**, 757 (1912).

⁶ Knorre, *Z. angew. Chem.*, **10**, 717 (1897).

⁷ Bricout, *Compt. rend.*, **118**, 146 (1894).

the presence of a slight excess of the corresponding acids gave deep red colorations, indicating oxidation of cerium but no precipitation. Prolonged boiling during electrolysis failed to hydrolyze the ceric cerium.

(2) **Precipitation of Ceric Phosphate.**—It is evident from the above results that ceric cerium can only be removed from an acid solution by the addition of an ion which will form an insoluble ceric salt. Cerium, in its tetravalent state, is very similar to zirconium and hafnium; in fact, it so characteristically resembles Sub-Group A of Group Four in the periodic table that cerium occupied the position now held by hafnium until the discovery of the latter. The phosphates of these quadrivalent metals are very insoluble. The addition of orthophosphoric acid or any of its salts causes immediate precipitation of ceric phosphate. The other rare earth phosphates are soluble in dilute mineral acids. Knorre⁶ and others have reported ceric phosphates for the purpose of analysis.

Ignited cerium group oxides were dissolved in concentrated nitric acid and diluted to make a 10% solution. Ignition of the oxides caused 90% of the cerium to be oxidized to the ceric state. This solution was heated to 80° and sodium phosphate solution slowly added. All of the ceric cerium was precipitated as phosphate in a heavy, flocculent form which settled well. The presence of 5% of free nitric acid prevented the precipitation of any of the other earths.

This ceric phosphate filtered well and could be washed free from the other earths. The filtrate was further treated with excess sodium phosphate and potassium permanganate slowly added. The cerous cerium still present was thus completely oxidized and removed as phosphate. Analysis of the filtrate showed the presence of less than 0.02% of cerium. The presence of this small amount of cerium is due to the slight solubility of the phosphate in nitric acid.

A 5% nitrate solution of the cerium group earths was then prepared having present 5% of free nitric acid and a slight excess of sodium phosphate. This solution was electrolyzed as described above. Ceric phosphate was thrown down as anodic oxidation took place. After prolonged electrolysis it was found that approximately 1% of cerous cerium remained in solution. This was evidently due to cathodic reduction. In another trial the cathode was surrounded by a porous cup. In a short time the cathode became coated with a gelatinous precipitate of ceric phosphate and electrolysis ceased. This method was then abandoned.

Ceric phosphate is a heavy, cream colored precipitate when thrown down from a hot solution with constant stirring. It is sparingly soluble in 5 *N* nitric acid. Very little solubility is indicated in nitric acid of less than 2.5 *N*. Ceric phosphate is very quickly decomposed with strong sodium hydroxide solution giving insoluble ceric hydroxide. This hydroxide filters well, can readily be dissolved in nitric acid and cerous oxalate precipitated from this solution by the addition of oxalic acid. A suspension of ceric phosphate in mineral acids may also be reduced to cerous phosphate by oxalic acid.

The above method was next tried on a large-scale laboratory or semi-commercial basis. Some two hundred kilos of commercial cerium group earths were treated in the following manner. The hydroxides were ignited in order to convert as much as possible of the cerium into the ceric state. A 10% nitrate solution of these oxides in the presence of 5% of free nitric acid was treated in 60-liter evaporation dishes. Phosphate precipitation

was carried out at a temperature of 80° , aided by mechanical stirring. Permanganate was then added until oxidation and precipitation of ceric phosphate were complete. The cerium free earths were precipitated from the hot filtrate as oxalates, utilizing the 5% of nitric acid present as optimum condition for oxalate precipitation. The ceric phosphate after thorough washing was treated with 50% caustic soda solution in an iron vessel. The ceric hydroxide was washed free from sodium phosphates, dissolved in nitric acid and the oxalate precipitated out.

It seemed possible that this phosphate method might also be used to separate the cerium and thorium together from cerium group earths. Monazite sand was accordingly "cracked" with concentrated sulfuric acid, the excess acid fumed off and the thorium and cerium earth sulfates were dissolved in water. The solution after acidifying with a little sulfuric acid was treated with potassium permanganate. Both thorium and ceric phosphates were precipitated together. The phosphate ion of the original monazite is thus utilized. To gain complete precipitation it was necessary to add a little more sodium phosphate.

Thus it is possible, where it is not of special interest to remove thorium separately, to obtain directly from monazite sand rare earths which have been freed of thorium and cerium by one precipitation.

(3) Discussion of Results

Anodic oxidation of cerium in sulfate and nitrate solutions goes to about 90% completion with no precipitation. Addition of an ion, such as the phosphate, allows 99% oxidation and precipitation of the cerium. If other oxidation methods are used, such as the addition of potassium permanganate, the cerium is entirely removed. The obvious reason for this complete separation is the immediate removal of the ceric cerium as an insoluble substance as soon as it reaches the ceric state. There is undoubtedly an equilibrium between the cerous and ceric states during an oxidation process. In other methods used this equilibrium is shifted mostly by excess reagents or heating, both of which require considerable time as well as reagents. In this method, however, such means are not necessary, for the presence of the phosphate causes immediate precipitation of ceric cerium as fast as it is formed. In this way the equilibrium is shifted practically completely toward the ceric ion, which is forthwith precipitated, giving complete separation.

The precipitation and removal of cerium in the form of ceric phosphate, as described in this research, has several practical points worthy of consideration. In both the chlorine and potassium bromate methods at least two treatments are necessary for the complete removal of cerium, especially in large quantities. The neutral permanganate method is slow, bulky and gives a precipitate which is difficult to filter and causes much

occlusion of the filtrate. Several days are required for complete reaction and a large quantity of potassium permanganate is necessary. In both the bromate and permanganate methods the excess acid which is present after dissolving the rare earths must be neutralized with calcium carbonate before the oxidation can be applied. For precipitation of the filtrate as oxalate, acid must again be added.

The phosphate method described gives 100% removal of cerium in one precipitation and is rapid. It takes a minimum of expensive oxidizing agents and the same acid concentration employed in the removal of cerium is that required for the precipitation of remaining earths as oxalates, saving time for neutralization as well as reagents. The use of the permanganate in acid solution also increases the efficiency. The neutral permanganate is only three-fifths as efficient as that used in the acid phosphate method. Also, in the acid solution, manganese dioxide is not formed in quantities to prove troublesome as in the neutral method.

It is undoubtedly possible to use other oxidizing agents for oxidizing the cerium to the tetravalent form for precipitation. It is also possible to remove thorium, zirconium and cerium completely, in one step, in the purification of rare earth ores. This should eliminate considerable time, as well as loss of rare earths and reagents, and prove a very efficient method.

Summary

Ninety per cent. oxidation may be accomplished anodically when applied to cerous sulfate or nitrate. Ceric chloride tends to decompose to cerous chloride and chlorine, so anodic oxidation is inefficient in this case. Separation of cerium is best accomplished by precipitation of a ceric compound. Addition of a soluble phosphate to a slightly acid solution of ceric nitrate causes the complete precipitation of the cerium as ceric phosphate. The other rare earth phosphates are soluble in the dilute acid. Thorium phosphate is also precipitated. Thus rare earths may be obtained free from cerium and thorium in one precipitation.

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The writer was born April 16, 1902, at Clymer, New York. He received his scholastic training in that place and was graduated from the high school there in 1919. That same year he entered Hope College, Holland, Michigan. In June, 1923, he received the degree of Bachelor of Arts from that institution. Matriculation in the Graduate School of the University of Illinois took place in September, 1923, and the degree of Master of Science was obtained in 1925. During the first three years at this institution the writer held the position of Graduate Assistant in Inorganic and Qualitative Chemistry; during the last year he has been a Fellow in Chemistry.



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